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INTERACTION OF RADIAL AND AXIAL DISPERSION IN LIQUID CHROMATOGRAPHY IN RELATION TO THE "INFINITE DIAMETER EFFECT"

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SUMMARY

The dynamics of radial dispersion of small solute samples injected centrally into a chromatographic column have been examined using a dual-electrode polarographic detector having one electrode fixed and the other movable radially across the face of the column exit frit. It is shown that the radial dispersion can be characterised by a reduced radial plate height, h_r , whose dependence on reduced velocity, v , obeys the equation

$$h_r = 1.4/v + 0.06$$

Experiments with trans-column injection using the same equipment show that there is little variation of peak-maximum velocity but that the mean axial plate height is increased up to threefold near the wall. The region of high dispersion extends about 30 particle diameters inwards from the walls.

Experiments with conventional high-performance liquid chromatographic columns and equipment, carried out with aromatic hydrocarbon solutes and columns of various lengths and bores packed with 21.5 μm spherical alumina, show that serious loss of efficiency occurs when solute can reach the wall regions. The data are consistent with the view that for efficient chromatography using microparticles the solute should not spread closer to the walls than about 30 particle diameters.

INTRODUCTION

In previous papers¹⁻³ it has been shown that column performance may be most effectively assessed by plotting the logarithm of the reduced plate height h ($= H/d_p$, where H = plate height and d_p = particle diameter) against the logarithm of the reduced velocity v ($= ud_p/D_m$, where u = mean linear eluent velocity and D_m = diffusion coefficient of solute in eluent). This method of representation permits easy comparison of data obtained using different columns, packing materials, solutes and

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eluent and sets readily remembered standards of good performance⁴. The dependence of h upon v can be interpreted in terms of Giddings' theories of peak dispersion⁵ using the semi-empirical equation

$$h = B/v + A v^{0.33} + C v \quad (1)$$

The (h, v) curves represented by eqn. 1 have minima which in practice occur at values of h between 2 and 5 and of v between 2 and 10. It has been shown both in practice² and in theory⁶ that optimum performance in chromatography using a given pressure drop is obtainable by adjusting the column geometry and particle size so that v is held around this minimum.

In eqn. 1 the first term arises from axial molecular diffusion, the second from velocity variations within the streaming part of the mobile phase, and the third from resistance to mass transfer between the streaming and static parts of the column (the latter comprising mobile and stationary phase held with the particles of the packing).

In 1969 Knox and Parcher⁷ pointed out that if the column diameter was sufficiently large in relation to the column length and particle diameter, solute molecules injected centrally onto the top of the column would fail to reach the walls in traversing the length of the column. If therefore additional peak dispersion arises due to wall effects, central injection into a sufficiently wide column should result in improved chromatographic performance. The general validity of this idea in true chromatographic systems has been fully vindicated by several studies⁸⁻¹⁰. However, no detailed examination of lateral dispersion and its effects on chromatographic performance have been reported.

As shown by Horne *et al.*¹¹, radial dispersion in a packed bed can be characterised by a radial plate height, H_r , defined as the rate of increase of the radial variance of the concentration profile with distance migrated:

$$H_r = d\sigma_r^2/dz \quad (2)$$

where σ_r is the standard deviation of the concentration profile and z is the distance measured along the axis of the column. For a point injection in a column of length L this is equivalent to

$$H_r = \sigma_r^2/L \quad (3)$$

The reduced radial plate height is then

$$h_r = H_r/d_p = \sigma_r^2/Ld_p \quad (4)$$

It has been established by chemical engineering studies reviewed by Horne *et al.*¹¹ that the velocity dependence of H_r may be expressed as

$$H_r = B D_m/u + A_r d_p \quad (5)$$

or in reduced terms

$$h_r = B/v + A_r \quad (6)$$

where B has the same significance as in eqn. 1 for axial dispersion and arises from molecular diffusion, and A_r represents the contribution to radial dispersion from stream splitting as the flow divides around particles of packing. From the chemical engineering studies and theoretical calculation it appeared that A_r lay between 0.1 and 0.2, and a value of 0.15 has generally been used in previous chromatographic work^{2,7-9}.

To ensure that a given column behaves as if it were of infinite diameter, it has been proposed⁷ that the column diameter d_c should exceed about four standard deviations of the radial dispersion, that is

$$d_c \geq 4 \sigma_r \quad (7)$$

Combining eqns. 4, 6 and 7 yields the condition for a column to be effectively of infinite diameter, namely

$$d_c^2/Ld_p \geq 16 B/v + 16 A_r \quad (8)$$

Eqn. 8 shows that some columns will behave as if of infinite diameter at values of v above a certain critical reduced velocity given by

$$v_{\text{crit}} = 16B/(I - 16A_r) \quad (9)$$

where I is the dimensionless parameter defined by

$$I = d_c^2/Ld_p \quad (10)$$

Taking $A_r = 0.15$ and $B = 1.8$ (a typical value for a porous packing¹²) eqn. 9 then gives

$$v_{\text{crit}} = 28.8/(I - 2.4) \quad (11)$$

For a typical column with $d_c = 5$ mm, $L = 0.25$ m and $d_p = 20$ μm , $I = 5$, and $v_{\text{crit}} = 11$. For the standard short column described later for which $L = 0.0825$ m, $d_c = 5.0$ mm, and $d_p = 21.5$ μm , $I = 14$ and $v_{\text{crit}} = 2.5$; this value of v_{crit} is sufficiently low that this column should behave as if of infinite diameter at all velocities which are of practical interest.

It must, however, be recognised that the onset of wall effects due to solute penetration into the wall regions will be gradual, and that any condition such as given by eqns. 7, 8, 9 or 11 must be quite diffuse. Furthermore, factors other than the rate of radial dispersion will determine the overall effect of walls on chromatographic performance. The shape of the injected sample will be clearly critical, and very different results may be expected from a centrally injected "point sample" and a uniform injection over the entire cross-section of the bed. Most practical injections will be of some intermediate and probably indeterminate type. Equally important will be the configuration of the packing close to the wall of the column, the "extent of wall region" (as a fraction of the total column cross-section), the linear velocity variations within this region, and their deviation from the mean over the column as a whole. We believe that the wall region can probably be thought of as extending a definite

number of particle diameters, say r particle diameters, from the column wall and that the "extent of wall region" can therefore be expressed as

$$\text{"extent of wall region"} = \frac{\text{area of wall region}}{\text{area of column}} = \frac{4r}{\rho}$$

where $\rho = d_c/d_p$, d_c being the column diameter. This view was first advanced by Knox and Parcher⁷ in order to explain why the (h, v) curves for glass bead columns were independent of ρ over the range $8 < \rho < 20$. They proposed that the wall region was about 3 particle diameters thick.

At present we know little about the "extent of wall region" in chromatographic columns with very large values of ρ (say $50 < \rho < 1000$) such as are used with micro-particles in liquid chromatography (LC), and we have very meagre data on whether peak migration rates differ between the wall regions and the core, or whether axial dispersion of solute migrating in the wall regions is significantly different from that for solute migrating in the core region. Finally, we have little information on whether, in a particular column, it makes any difference if solute is allowed to penetrate to the wall regions or not. Conceivably, the effects reported in support of the view that wide columns give better performance than narrow columns could be caused more by differences in the quality of packing achieved than by differences in the importance of wall effects, as is suggested by Wolf¹⁰.

It is the purpose of this paper to clarify some of these points.

The work falls into two more or less independent parts. In Part A, by using a dual polarographic detector with one electrode fixed and one movable radially across the face of the frit at the column exit we have determined the radial dispersion of centrally injected samples as a function of v in order to validate eqns. 5 and 6. Then, by making injections across the entire column cross-section we have measured the mean band velocity and the mean axial plate height as functions of distance from the column axis. The data give direct information about the thickness of the wall region.

In Part B standard chromatographic columns packed with 21.5 μm Spherisorb alumina were used. Dimensions were chosen so that v_{crit} fell within the experimental velocity range. The object of this part of the work was to determine the extent to which column performance deteriorated when solute was permitted to penetrate to the wall regions by reducing v . We examined two series of columns. In Series 1, the column bore and "extent of wall region" remained constant while I was varied by altering the column length. In Series 2, the length was kept constant while the column bore was altered, thereby changing both I and the "extent of wall region".

PART A — EXPERIMENTS WITH A DUAL POLAROGRAPHIC DETECTOR

Experimental

A high-pressure reciprocating pump (Orlita Giessen, Type DMP 1515) was used to pump the eluent, consisting of 0.1 M KCl kept free of oxygen by continual reflux under nitrogen. Pulsations due to the pump cycle were damped out by a 300-mm length of 5-mm bore stainless-steel tubing containing nitrogen which was teed into the flow-line between the pump and the injector head. The column, mounted vertically, was a glass tube 0.775 m in length and 11.7 mm in bore. A PTFE frit was

inserted into the outlet end and a stainless-steel ferrule was fixed to the inlet end with Araldite. This ferrule mated with an injector head fitted with a central guide which ensured that injections could be made strictly centrally into the top of the column packing. The general design of these fittings has been described elsewhere^{4,13}. The column was packed with clean dry glass beads by the rotate, bounce, and tap method (RTB-method)^{14,15}. The beads had a mean diameter of $64\ \mu\text{m}$ with a standard deviation of $3\ \mu\text{m}$ as found by microscopic measurement. The solute used was *p*-nitrophenol, which was dissolved in oxygen-free eluent. The value of D_m , used in the calculation of v , was obtained by the Wilke-Chang equation^{5,16} as $0.97 \times 10^{-3}\ \text{mm}^2\ \text{sec}^{-1}$.

The dual-electrode polarographic detector is outlined in Fig. 1. It consisted of two spherical platinum electrodes, 0.3 mm in diameter, melted on the ends of platinum wires. One electrode was fixed 0.5 mm from the column axis and the other could be moved radially by a micrometer across the face of the PTFE frit which retained the column packing. The two electrodes were positioned 0.1 mm below the lower surface of the frit. The platinum electrodes were sealed into glass sleeves and led out of a Perspex housing through 0.25-mm.-I.D. nylon tubing. They were held in PTFE plugs fitted into glass tubes which passed through PTFE plugs screwed into the sides of the housing. The platinum electrodes were maintained at a potential of $-1.0\ \text{V}$ relative to a mercury counter electrode which was an annular pool a few centimeters downstream of the Pt electrodes. The electrode currents were simultaneously recorded by a dual-pen recorder (Servoscribe Model RE 520.20) which measured the voltages developed across two resistors ($1\text{--}5\ \text{k}\Omega$ according to the working current) connected in series with the electrodes.

Radial concentration profiles were determined by injecting successive $5\text{-}\mu\text{l}$ portions of *p*-nitrophenol solution about 2 mm below the top of the bed of glass beads. This produced a near spherical injection about 2 mm in diameter. For the first injection the movable electrode was placed centrally, and for subsequent injections it was moved in successive steps of 0.5 mm towards the column wall. For each injection two concentration-time profiles were obtained, one from the reference electrode and

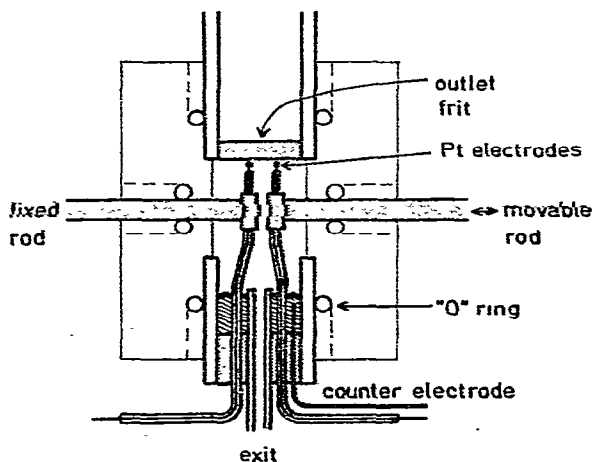


Fig. 1. Outline of the dual-electrode polarographic detector

one from the movable electrode. The area under each peak gave the amount of solute reduced at the electrode. The peak area obtained with the reference electrode was used to correct the areas obtained with the movable electrode for small variations in the quantity injected. The radial concentration profile was then obtained by plotting the corrected peak areas obtained with the movable electrode against the distance from the column axis after dividing each area by the corrected area for the axial position. Profiles were recorded in this way for several eluent velocities. Peak shapes were always Gaussian if the electrode was not less than 1.5 mm from the column wall, but became increasingly skewed and sometimes double when the electrode approached the wall.

Trans-column velocity and plate height variations were obtained by introducing solute samples across the entire column section. The eluent flow was first arrested and about 30 μl of a solution of *p*-nitrophenol in 1.0 M KCl was slowly and carefully injected just above the top of the bed of glass beads. Because of the higher density of the sample solution than eluent, the 30 μl sample quickly spread out as a thin layer about 0.3 mm deep over the top of the bed. When this was seen to have occurred the flow of eluent was restarted. Concentration-time profiles were again recorded at both electrodes for successive injections. By using the dual recorder it was possible to obtain accurate peak migration rates for different positions across the column, and to determine the plate height as a function of the radial position.

Results and discussion

Fig. 2 shows three plots of the radial distribution for 5- μl samples injected

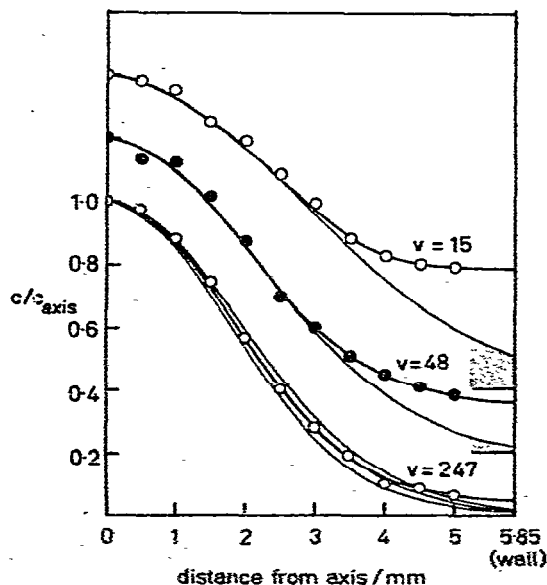


Fig. 2 Radial dispersion of a 5- μl sample of *p*-nitrophenol injected centrally into a 775 mm long \times 11.7 mm I.D. column packed with 64- μm glass beads. Distributions are shown for three reduced velocities. Gaussian curves are drawn to fit each of the three sets of data points, the upper two sets of which are displaced vertically. The lowest curve shows three Gaussian curves with $\sigma_r = 1.85, 1.90$ and 1.95 mm, respectively.

centrally at different flow velocities. At the highest velocity ($v = 247$) the solute barely reached the walls. The trans-column concentration distribution is Gaussian, as expected, and within experimental error follows the equation

$$c/c_{\text{axis}} = \exp(-x^2/2\sigma_r^2) \quad (12)$$

where c_{axis} is the concentration at the column axis, and c is the concentration at a distance x from the column axis. Three curves drawn through the lowest set of data points show that $\sigma_r = 1.90 \pm 0.05$ mm.

According to the theory of second moments, the final variance should be given by

$$\sigma_r^2(\text{tot}) = \sigma_r^2(\text{inj}) + \sigma_r^2(\text{col}) \quad (13)$$

where $\sigma_r^2(\text{inj})$ and $\sigma_r^2(\text{col})$ are the variances due to the injector and column processes, respectively. It is, of course, $\sigma_r(\text{col})$ with which eqns. 2 and 4 are concerned, but it is $\sigma_r(\text{tot})$ with which we are really concerned in eqn. 7. If the injected sample is regarded as a 2-mm-diameter sphere, then $\sigma_r(\text{inj})$ is equal to the radius of gyration of this sphere, that is 0.63 mm, and $\sigma_r^2(\text{inj}) = 0.4$ mm². We therefore obtain for the variance and standard deviation due to the column processes

$$\sigma_r^2(\text{col}) = 1.90^2 - 0.4 = 3.21 \text{ mm}^2$$

whence

$$\begin{aligned} \sigma_r(\text{col}) &= 1.79 \text{ mm} \\ H_r &= 3.21/775 = 0.0041 \text{ mm} \\ h_r &= 4.1/64 = 0.065 \end{aligned}$$

In the second curve of Fig. 2, for which $v = 48$, there is now some penetration of sample to the wall regions and reflection from the wall. By fitting the portion of the distribution out to 4.0 mm from the axis, we obtain $\sigma_r(\text{tot}) = 2.18$ mm and $\sigma_r(\text{col}) = 2.09$ mm. When $v = 15$ (uppermost curve), there is considerable penetration to the wall and $\sigma_r(\text{col}) = 2.68$ mm. The dependence of the reduced radial plate height upon reduced velocity is shown in Fig. 3. The best fit of eqn. 6 to the data is

$$h_r = 1.4/v + 0.060 \quad (14)$$

The value of $B = 1.4$ is, within experimental error, in agreement with the previous value of 1.2 obtained for axial dispersion in a bed of packed spheres by Knox and McLaren¹². The surprising result is the very low value of $A_r = 0.060$ obtained in this study, which is about half that derived from chemical engineering work¹¹. It is possible that the lower value now obtained is the result of our use of impermeable spheres rather than angular porous particles and further work using different packings would be required to clarify this point. The present value is also somewhat lower than that predicted theoretically on the basis of a simple stream-splitting mechanism¹¹.

Fig. 3 also shows the dependence of the axial plate height upon reduced velocity.

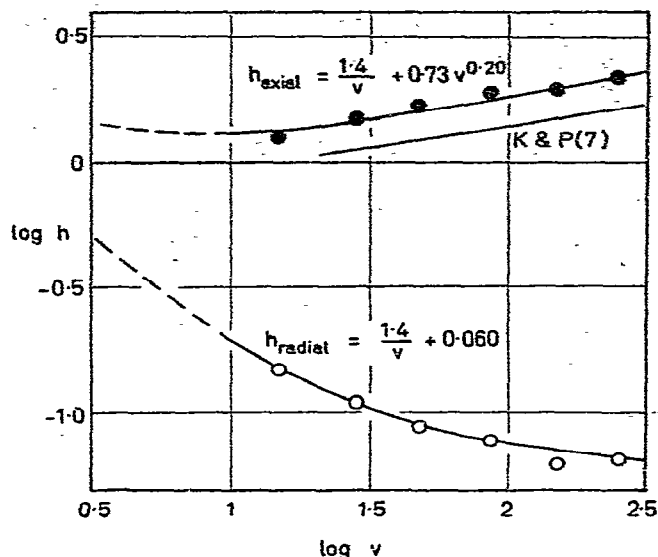


Fig. 3. Axial and radial reduced plate height-velocity plots. For column details, see Fig. 2. K & P (7) indicates data for 480- μ m particles obtained by Knox and Parcher⁷.

In agreement with Knox and Parcher⁷ h rises very gradually with v according to a low exponent of about 0.2 compared to the exponent of about 0.33 obtained with narrow columns. Fig. 3 also demonstrates the dramatic difference in the rate of axial and radial band spreading in chromatographic columns. Under conditions widely used in high-performance liquid chromatography (HPLC) with v around 20, h_{axial} is about ten times as large as h_{radial} . However, when $v = 1$, typically used in thin-layer chromatography (TLC), h_{axial} and h_{radial} are comparable. Thus, spots in TLC tend to be circular, while bands arising from point injections in HPLC are considerably elongated, the more so the higher the velocity.

Fig. 4 obtained using trans-column injections, shows concentration-time profiles obtained centrally and 1 mm from the column wall alongside the profiles obtained with the fixed electrode. In the first case the chromatograms (taken with the electrodes 0.5 mm apart) are essentially superimposable after allowing for the pen-displacement of the dual recorder. The traces in the second case differ markedly. The peak arising from the wall region emerges about 9 sec earlier than that from the reference position in a total elution time of 440 sec. It is also lower, wider and significantly asymmetric, showing considerable "fronting".

Fig. 5 shows how the velocity obtained from the peak maximum depends upon radial position. Surprisingly there is little evidence of a sudden upsurge in velocity near the wall. Indeed the main velocity variation occurs between 1 and 3 mm from the axis. This almost certainly results from the packing procedure, which either causes some fractionation of particles across the column or causes slight compaction towards the centre relative to the outer regions. The same result was obtained for different radial directions. There is therefore no evidence here of large velocity variations near the wall. However, the development of peak asymmetry as the wall is approached does

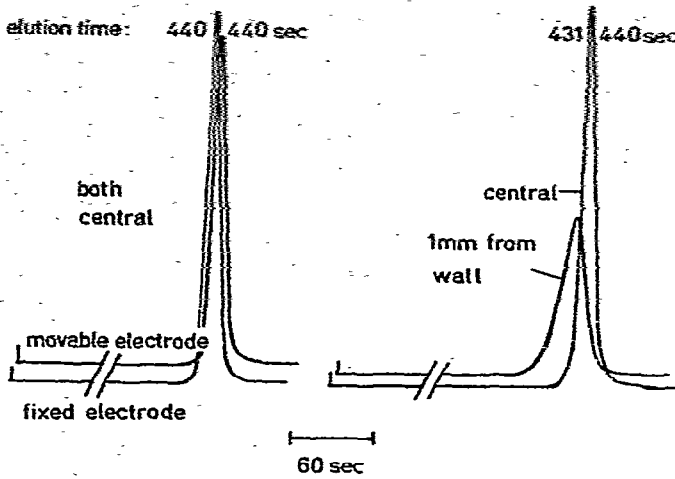


Fig. 4. Dual recorder traces for elution of a trans-column injection with the movable electrode placed centrally (left-hand trace) and 1 mm from the column wall (right-hand trace). The reference traces are taken by the fixed central electrode. For column details, see Fig. 2.

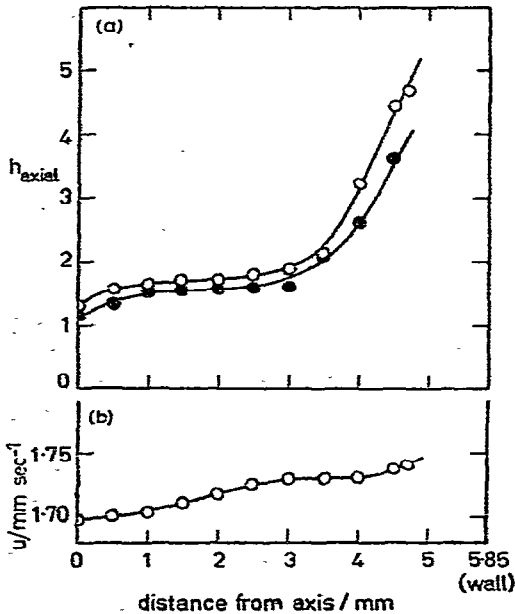


Fig. 5. Dependence of axial reduced plate height (a) and peak maximum velocity (b) upon radial position. O, Trans-column injection, $v = 115$; ●, central injection, $v = 15$. For column details, see Fig. 2.

suggest that the flow velocity very close to the wall is somewhat higher when averaged around any annulus than it is in the centre. In interpreting the data on both velocity variations and plate heights across the column, it is important to remember that the peak maximum velocity is not the same as the mean eluent velocity at any distance

from the axis because of radial mixing which will smooth out gross variation. Probably the most that can be said on the basis of the present data is that there may well be substantially increased velocities very near to the wall, as supposed by Knox and Parcher⁷, but that they extend only a very short distance into the packing proper, so that peak maximum velocities are little affected, although substantial peak skewing inevitably occurs.

The variation in plate height as a function of radial position also shown in Fig. 5 is much more dramatic; h rises from about 1.7 in the core region to about 4.7 at 1 mm from the wall. When the movable electrode was placed closer to the wall than 1 mm, severe peak distortion was noted with both peak shape and base width becoming irreproducible. Similar results were obtained from 5- μ l injections made centrally at flow velocities sufficiently low that a significant part of the sample reached the walls before emergence from the column. It is thus clear from Fig. 5 that serious band broadening and peak distortion begins to occur for solute emerging up to 2 mm from the wall, where there is virtually no disturbance of the mean peak velocity. Again lateral mixing will to some extent smooth out the variation in axial dispersion with distance from the column axis, but we believe that the effect will not be substantial and that the results shown in Fig. 5 imply that the region of disturbed packing extends much farther from the wall than we had previously imagined. We believe that the wall region in this column extends at least 1 mm into the column (≈ 15 particle diameters) and more probably about 2 mm (≈ 30 particle diameters). This is much farther than suggested by Knox and Parcher⁷, but their widest column had $q = 20$. It would now seem that there may be a thin layer of about $3 d_p$ in which wide velocity variations occur and also a much deeper region in which a highly dispersive packing arrangement is present, but without any gross variation in the mean velocity.

Further experiments are clearly required to obtain more information on the relationship between axial and radial dispersion near column walls. The most fruitful modification of the present experiment would be to use much shorter columns in which the extent of radial dispersion would be less so that the measured axial plate height at any distance from the column axis would be a better measure of the axial dispersive power of the column at that particular distance. It is also clear that experiments should now be carried out with porous and sorbing column packings so that the results are more directly related to real chromatographic situations.

PART B — EFFECT OF COLUMN GEOMETRY ON (h, v) CURVES

Experimental

The HPLC equipment was again home assembled. For moderate and high flow-rates an Orlita pump was used with a pulse damper as before; but for very low flow-rates the eluent was directly pressurised by nitrogen in a coil of nylon tubing. Detection was by a fixed-wavelength (254 nm) UV photometer (DuPont Model 410). All columns were made from normal heavy-walled glass tubing and were able to withstand at least 30 atm. Column end pieces and injectors were of brass and fixed to the glass by Araldite. They enabled injections of 0.5 μ l of sample to be made centrally into a 2-mm deep layer of 200- μ m-diameter glass beads on the top of the column packing proper. The eluent was hexane from which aromatics had been removed by passage through silica gel, and which had been degassed by reflux. Sample solutions were

made up from a selection of the following aromatic hydrocarbons dissolved in hexane: toluene, styrene, naphthalene, biphenyl, and anthracene. Their diffusion coefficients in hexane were taken as $3.3 \times 10^{-5} \text{ mm}^2 \text{ sec}^{-1}$.

Columns were packed with Spherisorb alumina, Type X, kindly gifted by the Material Preparations Unit, A.E.R.E., Harwell, Great Britain. Alumina Type X had a surface area of $200 \text{ m}^2 \text{ g}^{-1}$. The mean particle diameter of the spherical alumina particles was $21.5 \mu\text{m}$ with a standard deviation of $1.9 \mu\text{m}$, as found by microscopic measurement of about 100 particles.

Two different dry-packing methods were used, the "RTB" method previously described¹⁵ and a "vibrator" method, which was carried out as follows: a 10–20 mm depth of packing was slowly added to the column which was rotated at about 1 revolution per second. The tip of an engraving tool, vibrating at 50 Hz, was held against the glass column until no further settling of the packing occurred. Further layers of packing were added and the procedure repeated until the column was filled. This method has the attraction of simplicity and cheapness, but the technique of the operator is critical and considerable practice is required before reproducible results can be obtained. Crucial factors are the amplitude of the vibration of the tool, and the angle and manner by which it is held against the column. Once mastered, the technique produces columns which have the same efficiency as those produced by the RTB method. The main advantage of the RTB method is that it can be used successfully and reproducibly by operators with widely different experience in chromatography.

When using the RTB method to ensure efficient packing, it was necessary to standardise the activity of the alumina before packing the column. The alumina was first heated for 4 h at 400° to desorb water, 2% (w/w) of water was then added, and the alumina + water allowed to equilibrate overnight in a sealed bottle on a rolling machine. When using the vibrator method the alumina could be used without any pretreatment.

Results and discussion

The validity of eqn. 1 for fine-particle alumina was checked over an extended range of reduced velocity using a standard short column 82 mm long and 5.0 mm bore. Fig. 6 shows the data fitted by eqn. 1 with the following values of the constants A , B and C

Upper line: $B = 3.6$, $A = 0.4$, $C = 0.16$

Lower line: $B = 3.0$, $A = 0.4$, $C = 0.09$

It is noticeable in this and later figures that at high values of v , h increases as k' increases, while at low values of v , h is roughly independent of k' . This implies similar A and B values for all solutes but C values increasing with k' . This is in broad agreement with general experience in gas and liquid chromatography (see ref. 1, for example).

The minimum reduced plate height is around $h = 2$ at a reduced velocity $v = 5$. The curve clearly shows the upward trend in h due to molecular diffusion at low velocities, which is familiar to gas chromatographers.

For a porous solid the value of B is expected to lie between the value of 1.2 for random-packed impervious spheres and 2.0 for diffusion in a pure liquid¹². The value of about 3.3 is therefore unexpectedly high. There are three possible explanations,

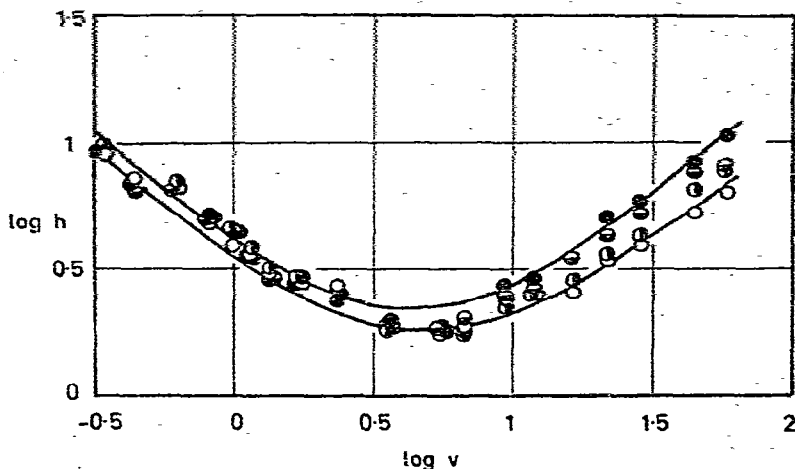


Fig. 6. Reduced plate height-velocity plots for 21.5- μ m Spherisorb Alumina X over a wide velocity range. Column, 82 \times 5.0 mm I.D. Solute samples: \circ , toluene ($k' = 0.5$); \ominus , styrene (1.0); $\textcircled{\bullet}$, naphthalene (2.3); \bullet , diphenyl (3.5). For upper and lower lines, see text.

viz. (a) The assumed solute diffusion coefficient is low by a factor of 1.6–2.0. We believe this to be unlikely. (b) Some diffusion occurs on the adsorbent surface. This would undoubtedly raise B (see ref. 4, for example), but, contrary to our data, one would then expect different values of B for the different solutes, whose values of k' ranged from 0.5–3.5. (c) At reduced velocities below about 2.5 (the value of v_{crit}) solute can reach the walls and therefore performance is likely to be impaired. An increase in h due to wall effects might therefore be expected at low values of v and in fitting eqn. 1 to the data this would show up as a larger B term. In view of the data which follow, this seems to be the most likely explanation.

The value of A is very low and equals the best value previously obtained, namely 0.4 for 480- μ m glass beads⁷. The very low value confirms the excellent packing characteristics of Spherisorb aluminas. The values of C on the other hand are somewhat higher than those previously found for porous materials, which were closer to 0.05¹. High C values suggest that mass transfer is relatively slow in Alumina X. However, the disadvantage of the higher C values is not a serious limitation if conditions are chosen so that one works at reduced velocities close to the minimum. This is best achieved by working with particles in the 5- or 10- μ m range rather than with 20- μ m particles^{2,6}.

For the further experiments on the effect of column geometry on (h, v) curves, the band shown in Fig. 6 is taken as the standard for a column in which there is negligible penetration of centrally injected solute to the walls at eluent velocities of practical significance (*i.e.*, at values of v equal to or greater than that for minimum h).

In Series 1, columns with $d_c = 5.0$ mm and $d_p = 21.5$ μ m were used with lengths varying from 82 to 280 mm. The columns were packed by the vibrator method and the test mixture contained toluene ($k' = 0.5$), styrene (1.0), naphthalene (2.3), and biphenyl (3.5).

In Series 2, columns with $L = 145$ mm were used, having bores from 2.3–7.0 mm. These columns were packed with deactivated alumina using the RTB method.

TABLE I

COLUMN PARAMETERS

Series 1: $d_c = 5.00$ mm; $d_p = 21.5$ μ m; vibrator packing method						
L (mm)	82	150	220	280	(485) [*]	(6 ⁰⁰) [*]
I	14.1	7.75	5.3	4.15	(2.4)	
g	235	235	235	235	(235)	(235)
v_{crit} (eqn. 11)	2.4	5.3	9.9	16.5	(∞)	
I'	7.75	4.27	2.91	2.29		(1.00)
v'_{crit} (eqn. 16)	4.25	8.8	15.1	22.3		(∞)
Series 2: $L = 145$ mm; $d_p = 21.5$ μ m; RBT packing						
d_c (mm)	7.0	5.1	4.2	3.2	(2.75) [*]	2.3
I	15.7	8.34	6.66	3.28	(2.4)	1.69
g	325	235	195	150	128	105
v_{crit} (eqn. 11)	2.2	4.8	6.8	33	(∞)	
I'	10.4	4.63	2.70	1.15		0.32
v'_{crit} (eqn. 16)	3.1	7.9	16.9	192		

* Asymptotic values of length and diameter at which v_{crit} becomes infinite.

For this less active alumina the test mixture was toluene ($k' = 0.3$), biphenyl (0.8), and anthracene (1.5).

The geometrical dimensions and characteristics of the nine columns used are given in Table I. For each column a value of v_{crit} can be calculated according to eqn. 11. These values are shown in Fig. 7. For columns which are sufficiently long (Series 1) or sufficiently narrow (Series 2) solute will always penetrate to the walls and limiting lengths and diameters therefore appear as asymptotes in Fig. 7.

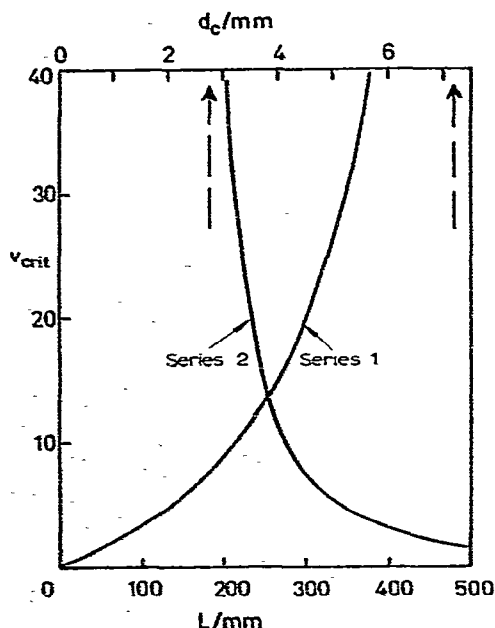


Fig. 7. Dependence of v_{crit} upon column length for 5-mm-bore columns (Series 1), and upon column diameter for 145-mm-long columns (Series 2), packed with 21.5- μ m particles.

Fig. 8 shows the (h, v) plots for the columns of Series 1. The plots are displaced vertically for convenience and in each case the band containing the standard data points of Fig. 6 is shown along with the values of v_{crit} calculated by eqn. 11. It is evident that the data obtained from the longer columns coincide within experimental error with those for the standard short column at high values of v , but deviate upwards at lower values of v . The break-away generally occurs at velocities somewhat above v_{crit} , as calculated by eqn. 11.

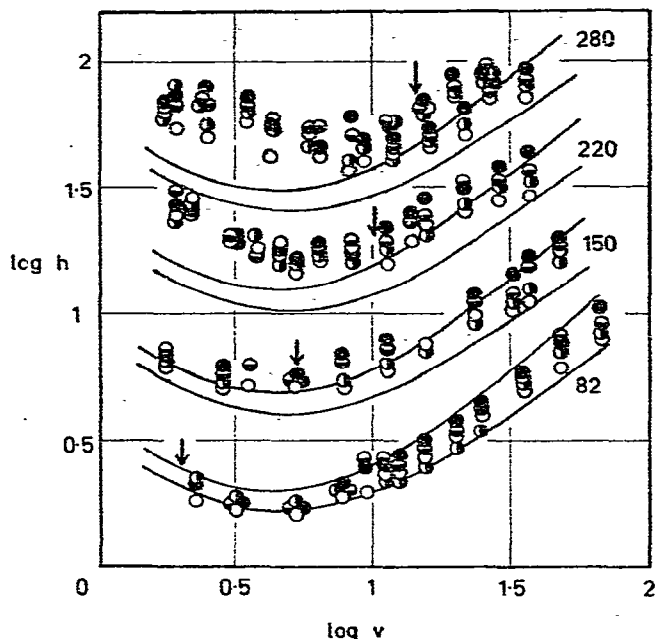


Fig. 8. Reduced plate height-velocity plots for columns of Series 1 (see Table I). Column lengths (in mm) are given for each set of data points. Solute identification, as for Fig. 6. Points for all but the lowest series are displaced vertically for clarity. The lines drawn show the position of the standard data of Fig. 6 in relation to the data for the other columns of Series 1. Arrows indicate the value of v_{crit} from eqn. 11.

These curves provide clear evidence that penetration of solute to the wall regions leads to higher plate heights and poorer performance. The observation that the plate height deteriorates for a given packing as the column is lengthened has been observed before and has generally been put down to the difficulty of packing long columns¹⁷. This explanation is unlikely to apply in our experiments since the columns were all packed dry and the bed should be packed in the same way at all depths.

Fig. 9 shows the equivalent data for the columns of Series 2. While the data show more spread between high and low values of k' , similar trends are apparent to those found in Series 1. For the 7-mm-bore column the (h, v) curve is in good agreement with that for the shorter 5-mm-bore standard column, which has a similar value of I . For the 5.0- and 4.2-mm columns of Series 2 the (h, v) curves again break away from the standard curve at velocities just above v_{crit} , calculated from eqn. 11. For the 3.2- and 2.3-mm-bore columns very different (h, v) curves are obtained. The data

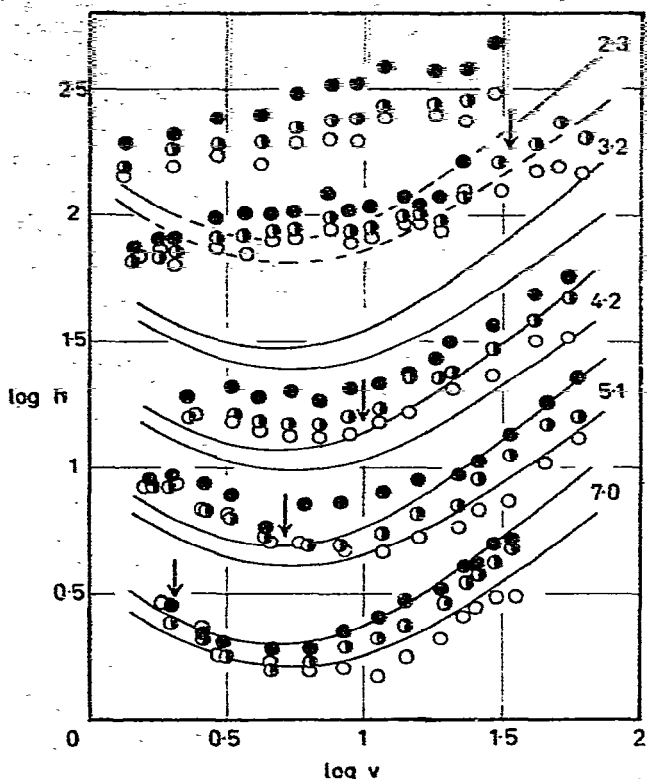


Fig. 9. Reduced plate height-velocity plots for columns of Series 2 (see Table I). Column diameters (in mm) are given beside each set of data points. Solute identification: \circ , toluene ($K' = 0.3$); \ominus , biphenyl (0.8); \bullet , anthracene (1.5). For significance of bands and arrows, see Fig. 8.

for the 3.2-mm-bore column are particularly striking, since this column has roughly the same I value as the 280×5 mm-bore column of Series 1, yet the (h, v) curve is almost the same as that for the 2.3-mm-diameter column, which, according to eqn. 11, can never behave as if of infinite diameter.

Two observations suggest that the use of eqn. 11 underestimates the importance of wall effects. Firstly, the (h, v) curves break away from the standard curve at velocities considerably above v_{crit} . Secondly, the 145×3.2 mm column behaves as if it could never show infinite diameter behaviour in spite of v_{crit} according to eqn. 11 being about 30. There are two ways in which such discrepancies could arise, viz. (a) The assumed value $B = 1.8$ could be too low (this would make all the values of v_{crit} too low), but as already argued, it is difficult to justify a value of B above 2. (b) The wall region may have a substantial thickness, as suggested by the results of Part A. The appropriate diameter to be used to calculate v_{crit} should then be not the column diameter d_c but the diameter of the homogeneously packed central core of the column. The results of Part A suggest that this core does not reach beyond $30 d_p$ from the wall. For $21.5\text{-}\mu\text{m}$ alumina this would produce a wall region about 0.65 mm thick. Thus the core diameter which should be used in calculating I for v_{crit} should be taken as 1.3 mm less than d_c .

Taking full account of the results of Part A using the new value of 0.062 for A_r and taking $B = 1.8$ for porous particles, the condition that a column exhibits no wall effects becomes

$$I' \equiv (d_c - 60 d_p)^2 / L d_p \geq 16 (1.8/v + 0.062) \quad (15)$$

We then obtain for v_{crit}

$$v_{\text{crit}} = \frac{28.8}{\frac{(d_c - 60 d_p)^2}{L d_p} - 1.00} \quad (16)$$

Table I compares the value of v_{crit} obtained from eqns. 11 and 16. Those from eqn. 16 are 50–100% higher for all columns, with one notable exception. For the 145×3.2 mm column v_{crit} is increased from 33 to the very high value of 192. For practical purposes this column can never be free of wall effects by eqn. 16.

The modification of the basic condition given in eqn. 7 to allow for a wall region of substantial thickness as proposed in Part A removes the two anomalies and so generally substantiates this proposal.

CONCLUSIONS

The major conclusion from this work is that the wall region in an otherwise well packed LC column extends about 30 particle diameters into the column. Within this region there is only a small increase in mean peak velocity but a drastic increase in dispersive power as the wall is approached. Thus penetration of solute into this region greatly affects column performance and in the worst cases can increase the apparent plate height threefold.

It therefore seems important to study methods for improving the packing characteristics in the wall region.

However, all effects can be avoided if a column is sufficiently wide. The condition for wall effects to be avoided which we now recommend is

$$d_c - 2 r d_p \geq 4 \sigma_c$$

which leads to

$$I' \equiv \frac{(d_c - 2 r d_p)^2}{L d_p} \geq 16 \left(\frac{B}{v} + A_r \right)$$

The recommended values of the constants are: $r \approx 30$, $B = 1.4$ (impervious particles), 1.8 (porous particles), and $A_r = 0.060$.

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